

*The Influence of the Constituents of the Crystal on the Form of the Spectrum in the X-ray Spectrometer.*

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The construction and use of the X-ray spectrometer have been described in previous papers.\*

It is found that the relative intensities of the various parts of a spectrum may be greatly altered by changing the crystal which is used in the spectrometer. The present paper contains an account of experiments made to determine the origin of this effect. It is shown that it may be ascribed to well known discontinuities in the relations between the atomic weight of an absorbing screen and its power of absorbing X-rays of given quality. This cause operates through the absorbing action of the atoms of which the crystal is composed.

It is convenient, in the first place, to describe briefly the form of the spectra emitted by anti-cathodes made of various materials. In the adjoining figure

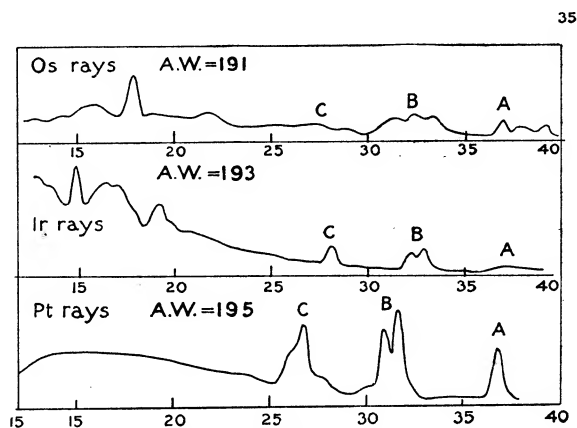


FIG. 1.

are shown the spectra of osmium,† iridium, and platinum, as given by the (111) plane of the diamond. The three allied metals here show certain common characteristics. Each spectrum contains, in the first place, a quantity of

\* 'Roy. Soc. Proc.' A, vol. 88, p. 428 ; vol. 89, pp. 246 and 276.

† Note added November 27.—A closer examination of the rays issuing from the osmium bulb shows that there are five similar triplets, the head of each being identical with one of the five platinum lines.

general radiation; radiation, that is to say, which varies continuously in wave-length over a certain somewhat indefinite range. It is clear that there is a considerable amount of such radiation for all angles of setting of the ionisation chamber which are less than about  $25^\circ$ . Possibly this general radiation may eventually be found to consist in part at least of bands of homogeneous rays, but the resolving powers of the spectrometer are hardly sufficient as yet to determine the point. It may be remembered that Moseley and Darwin,\* using an apparatus of high resolving power, did not succeed in separating it into definite constituents. It is not, however, with this general radiation that I propose to deal at present.

Each metal emits certain groups of characteristic homogeneous rays. The characteristic rays of platinum divide themselves obviously into three groups which in the original paper† were called A, B, and C; the latter two are really double, as subsequent experiments have shown. Moseley and Darwin determined their spacings with great precision. Osmium also has three groups placed in the same way as those of platinum, but, as might perhaps be expected from its lower atomic weight, they extend somewhat further into the longer wave-lengths. The iridium spectrum again contains three groups, placed in a somewhat similar fashion to those of its companion metals, but they are not very strongly marked. Attention may be directed to the very strong peak in the osmium spectrum at  $17.8^\circ$ . If the spectrum had been given by rock salt (100), the angle would have been  $13^\circ$ .

In fig. 2 are shown the spectra of palladium and rhodium. Their remarkable simplicity and strong similarity to each other are very noticeable. The crystal used is rock salt (100). The angles at which the lines occur are, in the case of palladium,  $10.4^\circ$  and  $11.8^\circ$ ; in the case of rhodium,  $11.0^\circ$  and  $12.6^\circ$ . The wave-length of the more intense palladium line is  $0.576 \times 10^{-8}$ , and of the more intense rhodium line  $0.603 \times 10^{-8}$ . As has already been explained, the precision of these lines and their remarkable intensity in comparison with the general radiation makes the rhodium and palladium bulbs of great service in the investigation of crystal structure.

Fig. 3 shows the spectra of nickel and copper. Here, again, there are two noticeable lines in each. They are of nearly equal intensity, but their relative spacings, strange to say, resemble closely those of the palladium and rhodium rays. The two copper lines are at  $28.6^\circ$  and  $32.0^\circ$ ; the nickel lines at  $31.2^\circ$  and  $34.6^\circ$ . If the spectra of the last four metals are compared it is seen that the wave-length increases as the atomic weight diminishes. The frequency is not quite proportional to the square of the atomic weight.

\* 'Phil. Mag.', June, 1913.

† 'Roy. Soc. Proc.', A, vol. 88, p. 428.

Possibly an exact relation of this kind might have been anticipated, as Whiddington has shown that the energy of the cathode ray required to excite an X-ray of given quality is proportional to the square of the atomic

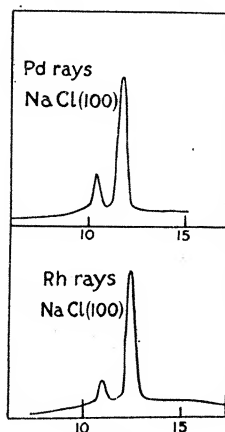


FIG. 2.

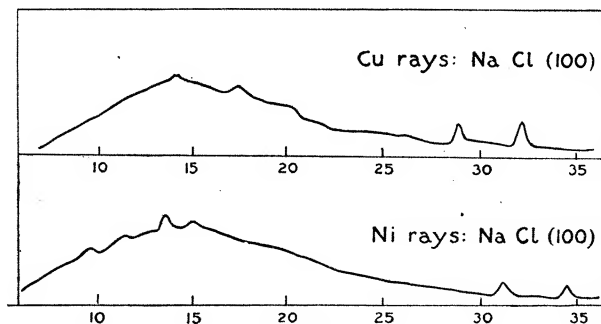


FIG. 3.

weight of the metal which emits that quality, and the quantum energy of the X-ray would be proportional to the frequency.

Spectra of silver and tungsten have also been obtained, but no very remarkable characteristic effects have yet been observed, except the existence of a small peak in the tungsten spectrum at 25.8.\*

It should be mentioned that the form of the spectrum is influenced not only by the nature of the radiator and the nature of the crystal but also by the circumstances of its production. Characteristic rays always occur in exactly the same place, but their relative intensities with respect to one another and with respect to the general radiation are modified by such causes as the nature and thickness of the glass wall of the X-ray bulb, by the width of the slits, narrower slits giving higher resolving power, and no doubt also by the general form of the X-ray bulb, its state of exhaustion, the nature of the coil, and so forth. The spectra which are shown above are therefore examples made under circumstances which need special definition before they can be fully interpreted. It is only the positions of the various peaks representing the wave-lengths of the characteristic rays which are invariable.

The spectrometer furnishes us with an arrangement of radiations in the order of the magnitude of their wave-lengths, and we are therefore able to make measurements on the relation between the wave-length and the absorbing powers of various screens.

\* 'Roy. Soc. Proc.,' vol. 89, p. 247.

From the work of Barkla we can anticipate the broad results of such measurements. In papers published at various times Barkla has shown that each metal emits characteristic homogeneous rays, and that the rays characteristic of any one metal can only be excited by rays characteristic of metals of higher atomic weight than its own. This is at least true as long as we deal with waves of one series as defined by Barkla. He has also shown that homogeneous X-rays are strongly absorbed by any substance in which they can excite the rays characteristic of that substance. If, for example, we consider the absorption of rays by a nickel screen we find that the absorption coefficient diminishes as the rays which we are considering are characteristic of chromium, iron, cobalt and nickel successively. Nickel itself is peculiarly transparent to its own rays. None of these substances are able to excite the characteristic X-rays of nickel; but if we pass on now to consider the absorption coefficient of nickel for the rays emitted by zinc, we find a sudden and very large increase. From this point onwards the absorption coefficient is of a higher order altogether, and though it again declines as the atomic weight of the radiator increases, it is evident that the coefficient has at a certain critical stage mounted to a much higher range of values. These facts are perhaps more easily expressed in terms of the results of the X-ray spectrometer, and it will be shown in a moment that the new experiments quite confirm them.

Let us for example suppose that we had an X-ray spectrum in which the energy was so distributed among the various wave-lengths that the form of the spectrum was the straight line AB in fig. 4. Now let us imagine

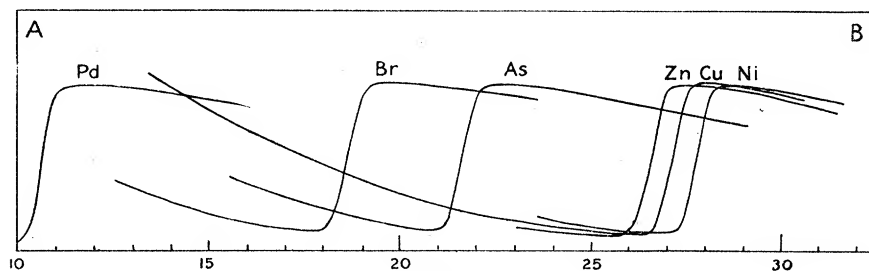


FIG. 4.

ourselves placing in turn various absorbing screens in the path of the rays and remeasuring the spectrum in each case throughout its entire length. The abscissæ in this figure are the angles of the ionisation chamber for rock-salt (100). The spectrum obtained after the insertion of a copper screen would be something of the form of the line marked "Cu" in the figure; for whereas copper rays are themselves (see fig. 3) emitted at angles  $28.6^\circ$  and

$32^\circ$ , these we know from Barkla's work must belong to the region of wave-lengths which are transmitted with particular ease, inasmuch as they cannot excite the characteristic radiations of copper, but for wave-lengths somewhat smaller than this we should expect a very marked increase in the absorption coefficient of copper, and this would be indicated by the sharp drop of the curve in the figure. The subsequent slow rise as the wave-length further diminishes is meant to represent the fact that after this stage has been passed the absorption coefficient once more diminishes with the wave-length.

Let us now proceed to consider actual experimental results. We cannot obtain a spectrum of the simple form of fig. 4, but we may use, for example, an osmium spectrum in which are represented waves of a large range of wave-length, though they may not all be represented to the same extent. In fig. 5 are shown the spectrum over a range between  $25^\circ$  and  $30^\circ$ , when

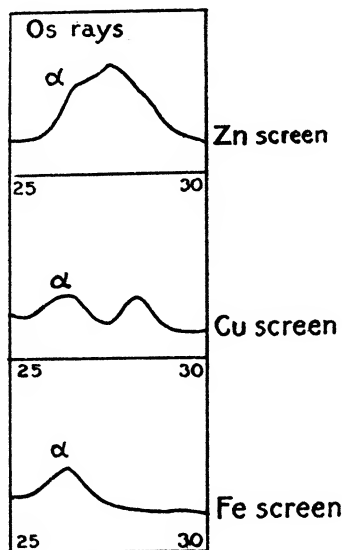


FIG. 5.

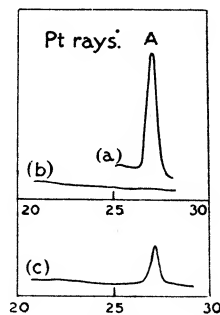


FIG. 6.

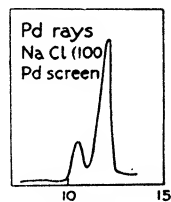


FIG. 7.

zinc, copper, iron screens are successively placed in the path of the osmium rays. Zinc is transparent in the higher order to practically all the wave-lengths within these limits. Copper is transparent in the higher order only to waves past  $27.5^\circ$ . The insertion of the copper screen has removed an important radiation at about  $27^\circ$ , transmitting easily the radiation of  $28.5^\circ$ . Iron is not transparent in the higher order to any wave-length within this radiation.

The peak marked  $\alpha$  appears in all three, but this is as it should be, for it is the second order spectrum of the strong osmium band at  $13^\circ$  and

possesses the penetrating power of that band. The penetrating power of the band at  $13^\circ$  is high because the wave-length is small. Though it lies on the wrong side of the critical points of the zinc, copper, and iron curves of fig. 5, it is far distant from those points. The same effect may be shown by the use of the rays from a platinum bulb. The platinum rays have a strong peak at  $27^\circ$ , which I have termed A on previous occasions. The figure (fig. 6) shows the spectrum of platinum between  $20^\circ$  and  $30^\circ$ , first when no screen is placed in the path of the rays, secondly when a zinc screen is placed in the path of the rays, thirdly when a copper screen is interposed. The figure shows that the zinc is relatively opaque to all rays at smaller angles than  $27^\circ$ , but transmits easily the strong radiation at that angle. Copper, however, is opaque to rays at  $27^\circ$  also. Thus the division between relative transparency and opacity is sharply marked; an atom of weight 65 transmits rays at  $27^\circ$ , and an atom of weight 63 does not. The same effect is illustrated again in fig. 7, which shows the effect of placing a palladium screen in front of the rays from a palladium bulb. It will be observed that, while the palladium rays themselves are transmitted in considerable quantity, all the rays to the left of the  $10^\circ$  are very largely absorbed.

Let us now pass on to consider what happens when the atoms in the crystal itself are such as to be relatively opaque to portions of the incident radiations. Fig. 8 (c) shows the spectrum of platinum rays reflected by a crystal of zinc blende. If we compare this with the form of the spectrum as given by rock salt (fig. 8, a), we observe that the peak A is very largely increased relatively to the peaks at B and C. From what has preceded a very simple explanation is at once forthcoming. The rays at  $27^\circ$  (in NaCl, or  $24^\circ$  in ZnS) which constitute the A peak penetrate the zinc with comparative ease; the rays at  $23^\circ$  and  $19^\circ$  (about  $20^\circ$  and  $17^\circ$  in ZnS) are very quickly absorbed by the zinc; consequently there is little opportunity for their energy to be scattered or reflected, since the great bulk of it is quickly taken up in other ways. These other ways we know from previous experiments to be wholly or at least in great part the conversion of X-ray energy into cathode ray energy. When the quality of the X-ray is such as to be able to excite the characteristic radiation in a substance on which it falls, there is at the

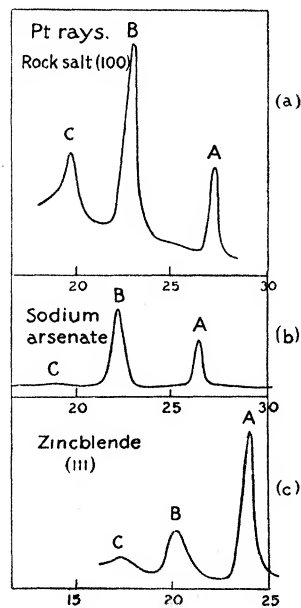


FIG. 8.

same time an unusually large expenditure of energy in the production of cathode rays.

An experiment such as that shown in fig. 8(c) above may be taken to indicate therefore that the scattering which is the basis of the reflection of X-rays does not display the same marked change as the absorptive coefficient does on passing through the critical value. Zinc blende gives a very large reflection of the peak A because the zinc is relatively transparent to the rays at  $27^\circ$ . In this region of the spectrum much less energy is spent in making cathode rays and there is much more available for reflection. There is no evidence as yet that the magnitude of the A peak as given by zinc blende is due to any special response of the zinc to the rays at that point; the effect is simply explained as a consequence of the peculiar absorption laws. We may test this hypothesis further in the following way. If we take crystals which contain an atom whose weight is somewhat larger than that of zinc we ought to find that the line of division between relatively high transparency and absorption has moved towards the left into the radiation of smaller wave-lengths. In fig. 8(b) is shown the spectrum of the platinum rays given by a crystal of sodium arsenate. Here it will be seen that both the peaks A and B are now strongly represented, but C remains still very small. The reason is that arsenic absorbs strongly all rays to the left of about  $22^\circ$  when the spectrum is given by NaCl (100); this is equivalent to about  $21^\circ$  in sodium arsenate. A crystal containing bromine, such as potassium bromide, allows rays to pass through which are short enough to include all the three groups of platinum or osmium. In the figure (fig. 9) is shown the spectrum of the osmium rays given by potassium

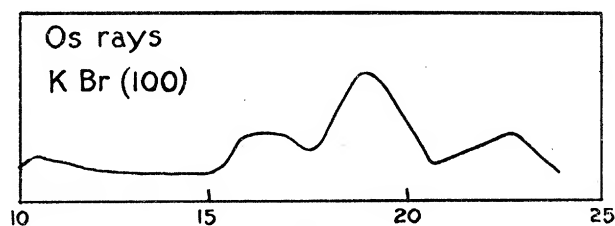


FIG. 9.

bromide and the three groups are now shown more nearly in their proper proportions. There should be a strong peak at  $10.5^\circ$ , namely that which occurs in the rock salt (100) spectrum at  $13^\circ$ , as has been mentioned already. This is almost completely destroyed in the present spectrum, for bromine is relatively opaque to the rays of that quality.

The main result of these experiments is to show the influence of the

weight of the atom in the crystal on the form of the spectrum. Within a region of atomic weight from 40 upwards, certain remarkable discontinuities of absorption occur in the manner explained above. When such atoms are present therefore in the crystal and the radiations divide themselves between those which lie on the one side of a critical point and those which lie on the other side, the spectrum will also show a sharp division at that point, being far stronger relatively on the one side than on the other. As to the influence of the weights of the atoms in a crystal when they are smaller than 40, we have still to take into account the very remarkable change in their absorption coefficients to all X-rays which occur when we pass from atoms of carbon and oxygen and so forth to atoms of aluminium or chlorine. Barkla has shown that aluminium absorbs all X-rays nine times as much as carbon, weight for weight. If the scattering power does not vary in the same abnormal way, then we should expect that a crystal of small atomic weight would be an exceptionally good reflector, on the same principle as before, that the less energy spent in absorption, the more there is available for scattering. We should expect, therefore, the diamond to give strong reflections apart from other reasons. This is well known to be the case. The diamond, moreover, gives reflections at far larger angles than other crystals. It must go a long way to explain this, that the spacings of the planes in the diamond are small, and therefore the spectra are thrown to wider angles, and also, that in a case where so much energy is spent in reflection, second-order spectra will be more obvious. It is quite possible that thermal agitation may have less influence on reflection intensity in the case of the diamond than in the case of other crystals, but these experiments show that good reasons for the peculiarities of the diamond reflection are already to be found in other directions.

It is very important to know the exact nature of the law connecting the atomic weight with the amount of scattering. The above experiments show that there are not the same abnormal variations in the amount of scattering as we proceed from lower to higher atomic weights as there are in the case of the absorption coefficients. Certain experiments which have been made by my son and myself indicate that the law is one of simple proportionality; that is to say, the amplitude of the scattered wave is proportional to the weight of the scattering atom. At any rate, certain results, to which I will now refer briefly, are very simply explained on this hypothesis.

A structure of the diamond, founded on measurements made with the X-ray spectrometer, has been explained in a recent paper.\* It was pointed out that the second-order spectrum given by the (111) plane disappeared in

\* 'Roy. Soc. Proc.,' A, vol. 89, p. 277.



consequence of the peculiar spacing of the planes. Zinc blende has the same construction as the diamond, except that the two interpenetrating lattices are composed of zinc and sulphur atoms respectively, and are therefore of different weight, while the two lattices of the diamond are both composed of carbon atoms, and are therefore of equal weight. The disappearance of the second-order spectrum referred to may be considered as due to an interference between the effects of the two lattices. When these two lattices are no longer of equal weight, the interference is incomplete, and accordingly the (111) spectrum of zinc blende gives a small second-order spectrum.

In the case of fluorspar, the first order spectrum of the (100) planes and the second order spectrum of the (111) planes have again disappeared, or very nearly so. In this case there are three lattices. The two fluorine lattices can be derived from the calcium lattice by equal simple translations in opposite directions along a cube diagonal; the amount of translation being a quarter of the length of the diagonal. The result is that the (100) planes contain calcium atoms and fluorine atoms alternately. There are two fluorine atoms to one calcium atom and therefore the weights in the planes are approximately equal, as in the case of the diamond. The disappearance of the first order spectrum indicates, therefore, that the conditions for mutual interference are satisfied when the weights are nearly equal, independently of the fact that in the one case the weight is due to calcium atoms and in the other to twice as many fluorine atoms. Weight alone and not atomic nature has determined the amount of scattering. The disappearance of the second order (111) spectrum is explained in the same way.

Other illustrations of the proportionality between scattering power and atomic weight are to be found in a comparison of the spectra of the various members of the calcite series. This point, with its bearing on the analysis of crystal structure, is more fully considered in a separate paper by W. L. Bragg.

Mr. W. L. Bragg and Mr. S. E. Peirce have kindly helped me to make some of the measurements referred to in this paper.

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